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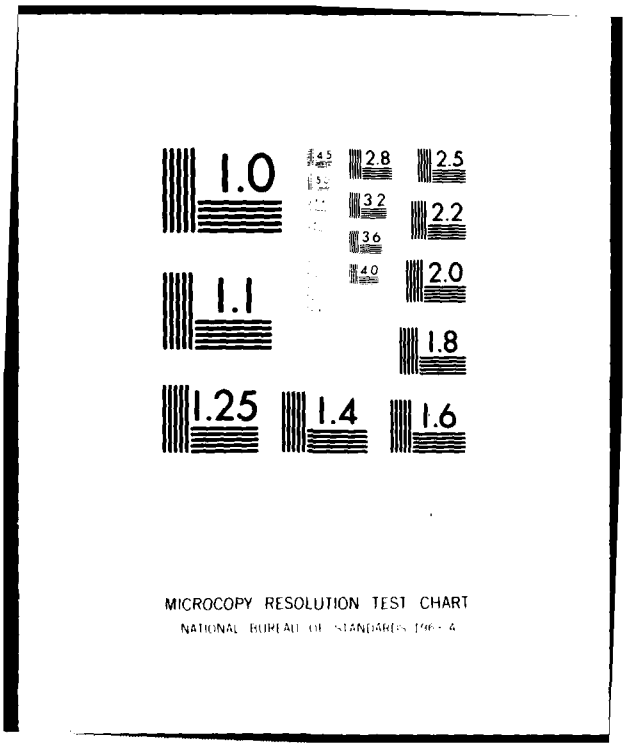
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The nitrogen 1s spectra have been investigated for a series of octaethylporphyrin and tetraphenylporphine complexes of lanthanides. The profile of N 1s spectrum for each lanthanide porphyrin showed that the four nitrogen atoms were equivalent in the complex. No significant change was detected between the N 1s binding energies of the lanthanide porphyrins. A good correlation between N 1s line width (FWHM) and a number of unpaired electrons in the complex was found. This result implies the presence of ex-

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(6) Nitrogen 1s Photoelectron Spectra of Octaethylporphyrin (OEP)- and Tetraphenylporphine (TPP)- Complexes of Lanthanides.

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Abstract: The nitrogen 1s spectra have been investigated for a series of octaethylporphyrin and tetraphenylporphine complexes of lanthanides. The profile of N 1s spectrum for each lanthanide porphyrin showed that the four nitrogen atoms were equivalent in the complex. No significant change was detected between the N 1s binding energies of the lanthanide porphyrins. A good correlation between N 1s line width (FWHM) and a number of unpaired electrons in the complex was found. This result implies the presence of exchange interaction between the ionized N 1s core and unpaired valence electrons which are delocalized into N valence shells. The spin density on the N atoms must originate from an overlap/covalent interaction between N and metal valence orbitals.

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Nitrogen 1s Photoelectron Spectra of Octaethylporphyrin (OEP)- and Tetraphenylporphine(TPP)-Complexes of Lanthanides

Sir:

X-ray photoelectron spectroscopy (ESCA) has been proved to be a powerful method for the elucidation of structure and bonding in complex molecules of f-transition elements.[1] In our previous work on ESCA spectra for a series of lanthanide(Ln)- and actinide(An)-compounds, $Ln(OH)_3$[2], $H[LnPc_2]$, and $AnPc_2$[3], we gave our attention to the satellite phenomena in Ln $3d_{5/2}$ and An $4d_{5/2}$ spectra. The observations suggested that f orbitals (either half-occupied or vacant orbital(s)) played an important role in the core ionization process which gave sharp variations in the satellite intensity of the spectra. As an extension of our ESCA study f-transition metal complexes, we now focus on lanthanide complexes of octaethylporphyrin Ln(OEP)(OH) [Ln=Eu,Gd,Yb, and Lu] and of tetraphenylporphine Ln(TPP)(AcAc) [Ln=Sm,Gd,Er, and Yb; AcAc=acetylacetonate].

We report here new findings derived from our observations of nitrogen 1s photoelectron spectra of Ln(OEP)(OH) and Ln(TPP)(AcAc). For a comparison, we measured also N 1s spectra of H_2TPP and H_2OEP. N 1s spectra have been shown to be a source of valuable information on the geometry of both porphyrins and metalloporphyrins.[4-8] Besides the geometrical viewpoint, we found a noticeable correlation between the line width (FWHM) of the N 1s signal and the number of unpaired electrons in the lanthanide porphyrin complexes. This indicates that unpaired valence electrons are not localized in the lanthanide 4f orbitals but are bound in MO's delocalized over N and lanthanide orbitals, and that the indued spin density on the N atoms provides an exchange interaction with the ionized N 1s core.

Octaethylporphyrin complexes Ln(OEP)(OH) have been prepared by Dr. T. Saran Srivastava. We synthesized and purified tetraphenylporphine complexes Ln(TPP)(AcAc) by the method described by C. -P. Wong, et al.[9] though the Sm compound seems to decompose gradually to metal-free TPP in chroloform. X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950 Å ESCA spectrometer

employing AlK_α X-ray excitation. The charging effects were neutralized by using an electron flood gun. The samples were prepared by carefully brushing each compound on double-stick scotch tape. We observed neither any visible evidence of decomposition nor change in the photoelectron spectra of the lanthanide porphyrins during the course of experiments preformed, except the case of Sm(TPP)(AcAc).[10] The spectra were calibrated using a C 1s binding energy at 284.8eV which arises from the carbon atoms having hydrocarbon character in the porphyrin rings.

The N 1s spectrum measured for either H_2OEP or H_2TPP exhibits a doublet due to the selective protonation of two of the central nitrogens. Observed binding energies of each doublet are 399.7eV and 397.7eV for H_2OEP and 400.0eV and 398.0eV for H_2TPP, and individual peaks have FWHM values of around 1.2_5eV. These binding energies are in agreement with those obtained previously by other groups [5,6,8] and differ only slightly from others which could be due to the use of different reference lines. We note here that our FWHM values (1.2_5eV) are close to the value 1.1eV given by Niwa et al.[5] which is the narrowest N 1s signal obtained for porphyrins in the solid state. This seems to warrant the subsequent discussion concerning the N 1s line width of lanthanide porphyrins.

In complexing a lanthanide ion with OEP or TPP, the N 1s spectrum collapses to a single peak with a binding energy value directly in between the corresponding porphyrin doublet. This is schematically drawn in Figure 1, where the N 1s spectra of free-base and metal-incorporated porphyrins are typified by those of H_2OEP and of Yb(OEP)(OH), respectively. The single N 1s peak indicates the existence of four equivalent nitrogens in the lanthanide porphyrins and thus the equalized four Ln-N interactions. The situation is achieved only when a lanthanide is located equidistant between the four nitrogen atoms.

Figure 1

The binding energies and the FWHM values determined for a series of lanthanide porphyrins are summarized in Table 1. No significant difference in the binding energies can be seen between the lanthanide porphyrins studied, indicating that the electronegativities of lanthanides are very similar to each other. The observed binding energies are somewhat higher than a value anticipated from the general-belief that a Ln-ligand bond has strong ionic character, and are even close to values obtained for metalloporphyrins of d-transition elements.[5] The result seems to imply the presence of some covalent character in Ln-N bond[11] similar to a M-N bond in d-transition metal complexes.

(Table 1)

As shown in Table 1, the FWHM changes noticeably from 1.3_8 to 1.9_1eV in the Ln(OEP)(OH) series and from 1.3_5 to 1.7_7 in the Ln(TPP)(AcAc) series, respectively. The most striking broadening of the N 1s peak in either of the series was observed for the Gd complex (f^7). We now see a correlation between the FWHM of the N 1s peak and *the number of unpaired electrons in the complex.* This is shown in Figure 2.

The most plausible interpretation of the broadning is multiplet splitting of the N 1s core level arising from an exchange interaction between the ionized core and unpaired valence electrons induced on the nitrogen atoms. Multiplet splitting of core-level peaks has been reported for inner 3s and 3p levels of d-transition metals[13,14] for 4s and 5s levels of lanthanides,[15] and for 1s levels of NO and O_2.[16,17] In every case the magnitude of the multiplet splitting (ΔE) of core s orbitals was found to be in good agreement with approximate theoretical estimates based on the equation[17,18]

$$\Delta E \simeq f_i H^i (2S + 1) \qquad (1)$$

where fi is the fraction of an unpaired electron on the i-th

atom, H^i denotes the core s electron-valence electron exchange integral, and S is a total spin. Among compounds of a similar type like Ln(OEO)(OH) or Ln (TPP)(AcAc) series, f_i may be considered to be constant throughout the series. Thus, the magnitude of the multiplet splitting ΔE simply correlates with total spin, i.e., the number of unpaired electrons of the compound in question. Unfortunately, we could observe a level broadening instead of a level splitting which is expected from the exchange mechanism. Nevertheless, eg. 1 seems to provide well a theoretical verification of our interpretation for the correlation obtained between the N 1s FWHM and the number of unpaired electrons.

The unpaired electrons on N atoms must be induced from half-occupied Ln 4f levels through a direct or an indirect interaction between N valence and Ln 4f orbitals. Possible mechanisms which cause spin polarization at the ligand site in f-transition metal complexes are (1) direct delocalization of f electrons into vacant ligand MO's[20,21] (2) charge transfer from filled ligand MO's to vacant metal f orbitals[21], or to metal outer 6s, 6p, or 5d orbitals,[22] (3) similar charge transfer from ligand to half-occupied metal f orbitals, and (4) interaction of ligand orbitals with filled metal orbitals which is exchange polarized by the f shell.[23] Mechanism (1) induces unpaired spin on the ligand which is polarized parallel to that of the f shell, while (2), (3), and (4) give antiparallel spin. From only the ESCA results, we cannot conclude which mechanism is responsible for the spin polarization on the N atoms in Ln(OEP)(OH) and Ln(TPP)(AcAc). However, our ESCA study implies strongly the presence of overlap/covalent interaction of lanthanide 4f and/or outer (6s,6p,5d) orbitals with N valence orbitals.

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10. For Sm(TPP)(AcAc), an additional peak appeared at around 1.8eV above the main N 1s signal at 398.0eV and the intensity of the peak relative to the main N 1s line was increased with a passage of time under x-ray irradiation. The additional peak seems to arise from pyrrole-type nitrogens in H_2TPP indicating that Sm(TPP)(AcAc) is decomposed by x-ray irradiation.

11. The "covalency" does not necessarily mean f-orbital participation in bonding. Lanthanide atoms have also outer 5d, 6s, and 6p orbitals which can effectively interact with ligand orbitals.[12]

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19. The multiplet splitting of N 1s peak measured for NO and di-t-butyl-NO radicals are 1.412eV and 0.539eV, respectively.[17] The magnitude of broadenings of N 1s peaks for Gd(OEP)(OH) (+0.5$_3$eV relative to Lu(OEP)(OH) and for Gd(TPP)(AcAc) (+0.4$_2$eV relative to Yb(TPP)(AcAc)) seems to be in the range of values which can be anticipated from multiplet splitting.

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Table 1 N 1s Binding Energies[a] and FWHM[b] of Ln(OEP)(OH) and Ln(TPP)(AcAc) (in eV)

	Binding Energy	FWHM
Eu(OEP)(OH)	398.1	1.7_7
Gd(OEP)(OH)	398.2	1.9_1
Yb(OEP)(OH)	398.2	1.6_0
Lu(OEP)(OH)	398.1	1.3_8
Gd(TPP)(AcAc)	398.0	1.7_7
Er(TPP)(AcAc)	398.4	1.4_3
Yb(TPP)(AcAc)	398.3	1.3_5

[a]Referred to C 1s = 284.8eV

[b]The full widths at half-maximum of photopeak

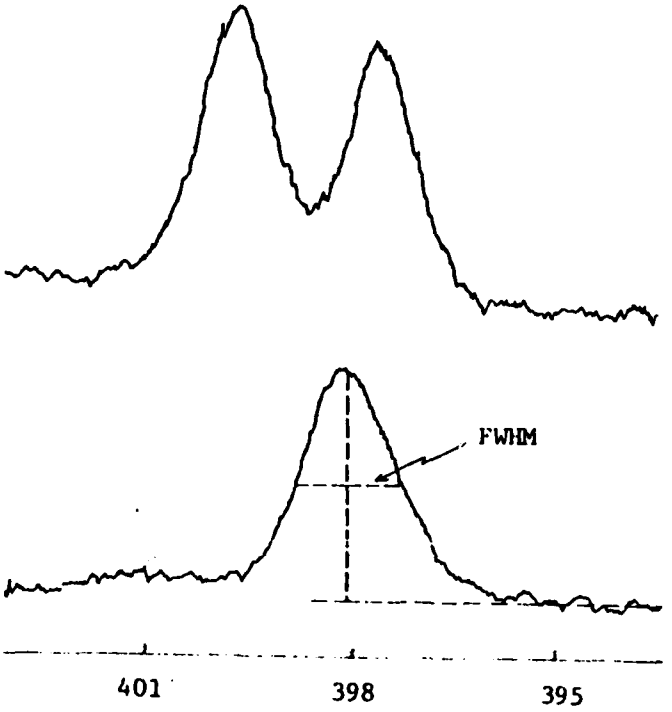

Figure 1. Typical N 1s signals of free-base prophyrin (top) and lanthanide porphyrin (bottom). The FWHM of a N 1s peak for each lanthanide porphyrin was estimated with a procedure shown by broken lines.

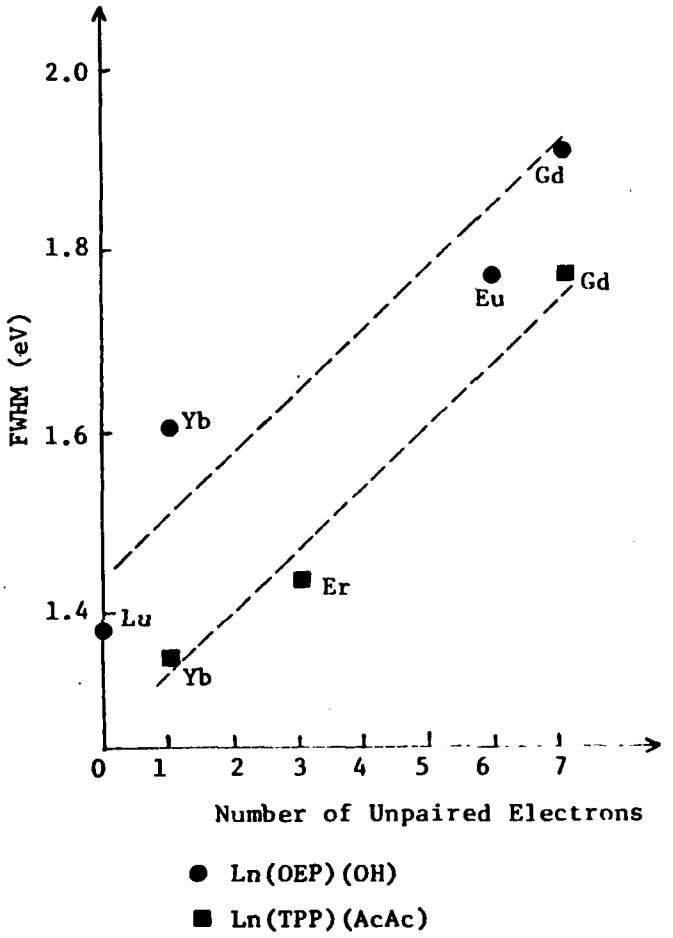

Figure 2. The line widths (FWHM) of N 1s peaks plotted against the number of unpaired electrons in the complexes.